Chain Length Effects on Aqueous Alkane Solubility Near the Solvents Critical Point

Eric M. Yezdimer[1,2,*] , Ariel A. Chialvo[3,4] and Peter T. Cummings[2,5]

[1] Department of Chemistry, University of Tennessee, Knoxville, TN, 37996.
[2] Chemical Technology Division, ORNL. Oak Ridge, TN, 37831-6268.
[3] Chemical and Analytical Sciences Division, Oak Ridge, TN, 37831-6110.
[4] Department of Chemical Engineering, University of Tennessee, Knoxville, TN, 37996.
[5] Departments of Chemical Engineering, Chemistry and Computer Science, University of Tennessee, Knoxville, TN, 37996.

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Abstract

Free energy of hydration calculations of butane and octane were conducted at several different state points. A relativity new method of performing the alkane insertion was used and it was found to perform quite well. Our preliminary simulation results are in good agreement with the recent equation of state predictions of Yezdimer et al. and suggest that at near critical conditions the solubility trends as a function of temperature for a series of alkane chain molecules may reverse.

*- To whom correspondence should be sent

Introduction

Accurate knowledge of the chemical potentials for organic molecules in aqueous systems at high temperature and pressure play a vital role in understanding many industrial, geochemical, and biological processes. Over the past few years there has been considerable advancements made in the development of accurate equations of state (EOS) for aqueous electrolytes and non-electrolytes at elevated temperatures and pressures. A recent work by Yezdimer et al. [1] has extended the EOS proposed by Sedlbauer et al.[2], based on Kirkwood's statistical mechanical theory of solutions[3], by including a simple functional group addivity scheme which allows for predictions of a wide variety of simple acyclic organic molecules to be made. While this equation performs very well at temperatures under 550 K, further analysis of several different classes of organic compounds show an unexpected shift in their solubility near the critical point. These shifts in the free energies of hydration imply that larger, longer chain molecules (such as hexane) have higher solubilities then smaller, shorter chain molecules (such as propane or butane). Since experimental data on aqueous organic compounds near the critical point are limited and/or are often difficult to obtain experimentally, we have chosen to employ computer simulations (molecular dynamics) in an effort to further explore the EOS's predicted behavior.

Simulations

In an effort to confirm this possible unintuitive behavior in the solubility, we have used molecular dynamic simulations to calculate the free energy of hydration, ΔG^{hyd}, for two alkane molecules (butane and octane) at several different state points. By performing

the calculations at infinite dilution one can obtain the Henry's law constant, k_H, through the equation [4],

$$\ln k_H = -\Delta G^{hyd} / RT + \ln \rho RT , \qquad (1)$$

where R is the ideal gas constant, T is the absolute temperature, ρ is the density of the pure solvent, and ΔG^{hyd} is given by Ben-Naim's [5] definition. For the alkane solutes we have chosen the united atom model of Martin and Siepmann [6] (TraPPE). The water solvent was modeled using the TIP4P-FQ fluctuating point-charge model of Rick et al. [7] For the unlike Lennard-Jones pair interactions, the Lorentz-Berthelot [8,9] combining rules, $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$ and $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$, were used.

The liquid-vapor coexistence curve for the TIP4P-FQ model has been determined by two independent studies. The Gibbs-Duhem integration [10] calculation of Yezdimer and Cummings [11] produced critical constants that are in good agreement with the Gibbs Ensemble [12] calculations of Chen et al.[13]. In this study we have taken the critical points of the TIP4P-FQ model to be T_c = 570 K, ρ_c = 300 kg/m^3 and P_c = 19 MPa.

Infinite dilution simulations of both butane and octane were performed in the NPT ensemble, using 256 and 512 TIP4P-FQ water molecules, respectively. Five different state points were examined for both butane and octane (T_r = 0.685, 0.830, 0.974, 1.031, 1.175; P_r = 1.28). Bulk conditions were reproduced using periodic boundary conditions and the electrostatic interactions were handled by Ewald summations[14,15]. A cut-off radius for the Lennard-Jones interactions (equal to ~ L/2) was used and the energies were then corrected for the truncation by assuming the radial distribution function at distances greater than the cut-off was equal to unity. The cut-off for the real component of the Ewald sum was taken to equal to that of the Lennard-Jones cut-off radius. A Hoover-

Nosé thermostat[16] and Andersen barostat[17] were used to maintain a constant temperature and pressure. A time step of 0.001 picoseconds was used and all simulations were carried out using a modified version of the DL_POLY software[18]. Each simulation run was allowed to equilibrate ~ 100 picoseconds and a thermodynamic integration (TI) technique[19] was used to calculate the free energies of hydration.

Each alkane molecule was grown into solution in one complete step, instead of the more common piece-wise fashion[20,21]. Müller and Paul [22] have shown that a single step TI method can be very efficient when dealing with long chains, although their calculations were performed only on lattice models and were restricted to examining the effect of excluded volume. This method has the advantage of being simpler (no dummy atoms and/or alchemical of molecular species are required) and can potentially produce a lower systematic error because there is no propagation of errors for each chain bead. The one possible major disadvantage of this approach is that it may suffer from sizable time-lag hysteresis, although we found no evidence of any significant time-lag errors [23].

As defined by Ben-Naim[5], the free energy of hydration can simply be related to the standard TI as follows,

$$\Delta G^{hyd}(T,P) = \int_0^1 \left\langle \frac{fU}{f\lambda} \right\rangle_{\lambda,T,P} d\lambda \qquad (2)$$

where U denotes the total intermolecular interaction energy of the system and only the solute-solvent Lennard-Jones intermolecular interactions are coupled as a function of λ. As such Eqn (2) describes the free energy difference between the solute in the ideal gas state (λ=0; $U^{LJ}_{TraPPE,TIP4P-FQ} = 0$) and the solute in the solution (λ =1). Since our simulations only contain a single alkane molecule, the integration of Eqn (2) yields ΔG^{hyd}

at infinite dilution. There is no need for any additional corrections due to the chain size and/or structure of our solutes[24], because any additional solute rotational-solvent interaction coupling energy is already included in the value of ΔG^{hyd} through the indicated average, $\langle \ldots \rangle_{\lambda}$.

Each TI consisted of 11 windows at λ = 1.0, 0.8, 0.6, 0.4, 0.3, 0.25, 0.2, 0.15, 0.10, 0.05 and 0. In an effort to avoid singularities[19,25] that can arise when a linear coupling scheme is used with the Lennard-Jones interactions, we have chosen to employ the non-linear coupling scheme proposed by Beutler et al.[26] For state points where $T < T_c$, every window was allowed to equilibrate 30 picoseconds and averages of $dU/d\lambda$ where taken for 70 picoseconds. At state points were $T > T_c$, each window was averaged for 110 picoseconds to ensure accurate sampling. The calculated curves for $dU/d\lambda$ versus λ where found to be well behaved (Figure 1) and were qualitatively similar to those discussed by Beutler et al. These curves were then integrated using the trapezoidal rule, and the results are presented in Figure 2.

Discussion

Our preliminary simulation results for $\Delta G^{hyd}(T,\rho)$ are given in Figure 2 and appear to be in good qualitative agreement with EOS predictions of Yezdimer et al. The reversal in the ΔG^{hyd} trends can clearly be seen in the vicinity of 630 K. Thus, in the region from ~630K – 670K, it requires less free energy to insert an octane molecule into solution than it does to insert a butane molecule. This behavior is exactly the opposite of the classical physical picture of solvation that one may normal envision, namely that a larger molecule

of similar solute-solvent interactions should possess a higher ΔG^{hyd} due to the larger cavity volume required. It is tempting to simply connect these shifts in solubility with the increased solvent compressibility near the solvent's critical point, however this possible affect has not yet been rigorously quantified and Chialvo and Cummings[26,27] have shown that the solvation free energy is independent of any long-range compressibility driven divergent behavior. However, the re-reversal of the trends for ΔG^{hyd} in the supercritical region can be explained [25] (due to the low solvent density) in terms of the temperature dependence [29] of the second cross virial coefficient [30]. It was also found that better agreement between the EOS of Yezdimer et al. and our simulations results could be obtained, particularly in the higher density region, by employing a more accurate form for the unlike Lennard-Jones interactions than the Berthelot Lennard-Jones combining rule [25,31] and the classical _ classical form of the free energy perturbation method of Wood et al. [32].

Conclusions

In this paper we have used a relativity new method for performing alkane insertion into solution and found that our preliminary molecular dynamic simulations qualitatively reproduce the reversal in the Henry's constant predicted by Yezdimer et al. This suggests that predicted reversal in solubility may in fact represent a real phenomena and is not simply a numerical artifact of Yezdimer et al.'s empirically fitted EOS.

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Summary of symbols

T – Temperature

T_c – Solvent critical temperature (T_c = 647 K for pure water)

T_r- Reduced temperature

ρ – pure solvent density

ρ_c– Solvent critical density (ρ_c = 322 kg/m^3 for pure water)

P - Pressure

P_c – Solvent critical pressure (P_c = 22 MPa for pure water)

P_r – Reduced pressure

R – Ideal gas constant

U -Total configurational energy

ΔG^{hyd} – Free energy of hydration

k_H – Henry's constant

L- Length of simulation box

λ – coupling parameter

σ – Lennard-Jones size parameter

ε – Lennard-Jones energy parameter

FIGURE CAPTIONS

1) Example of $\langle dU/d\lambda \rangle$ for octane (aq) at T_r=0.830, P_r= 1.28.

2) ΔG^{hyd} for octane (aq) and butane (aq) as a function of temperature. OOO- Simulated octane(aq); ΔΔΔ- Simulated butane(aq); ___ - Predicted octane(aq); _ _ _ - Predicted butane(aq) (Yezdimer et al. [1], T < 630 K; Second cross-viral coefficients [29,30], T > 660 K). The error in ΔG^{hyd} was found to be on the order of 1 – 1.5 kJ/mol for both octane(aq) and butane(aq). For clarity, the error bars are shown only on the octane(aq) points.

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Figure 1

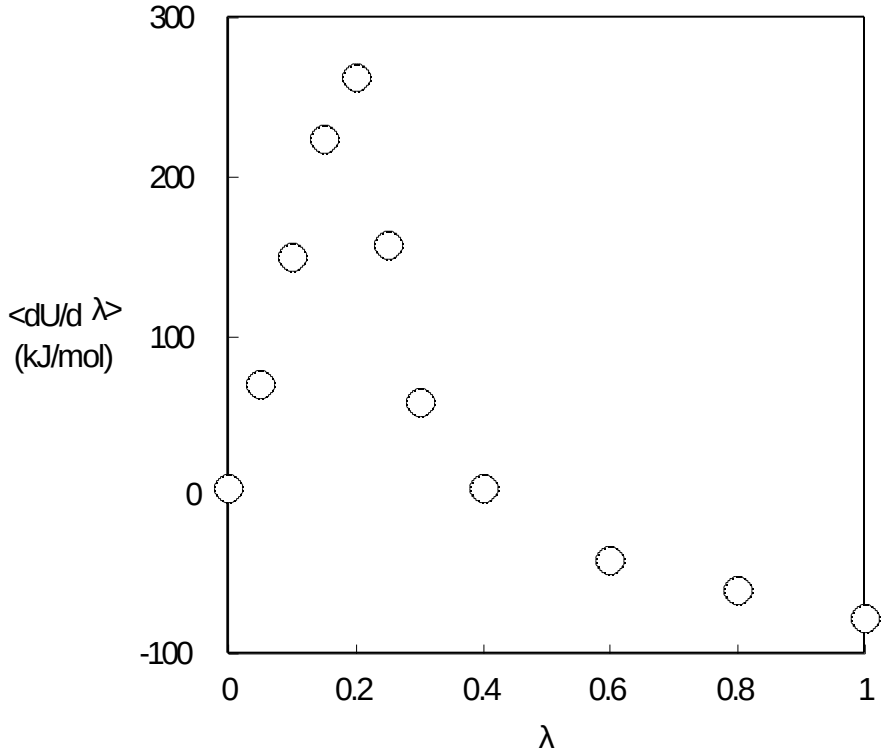

Figure 2